THIN LAYER ADSORBENT FOR THE REMOVAL OF METHYLENE BLUE VIA BRUSHING, AIRBRUSHING AND ELECTROSPINNING

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by

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LIST OF SYMBOLS

q_e	Adsorption capacity (mg/g)
Qm	Maximum adsorption capacity of adsorbent (mg/g)
K_L	Constant of Langmuir isotherm (L/mg)
C_i	Initial concentration (ppm)
C_f	Final concentration (ppm)
K_F	Freundlich isotherm constant (mg/g) $(L/mg)^{1/n}$
1/n	Adsorption intensity or factor of heterogeneity
ppm	Parts per million
β	Dubinin-Kadushkevich constant
$\in$	Polanyi potential
R	Universal gas constant (8.314 J/mol.K)
E	Mean adsorption energy
T	Absolute temperature
b	Temkin constant that is related to the heat of sorption (J/mol)
A_T	Temkin isotherm constant (L/g)
C_e	Equilibrium constant of adsorbate (mg/L)
°	Degree of angle
V	Volume
m	Mass
%	Percentage
rpm	Revolution per minute
k_1	Pseudo-first-order

LIST OF ABBREVIATIONS

AC	Activated carbon
EDX	Energy dispersive X-ray
FTIR	Fourier transform infrared
MB	Methylene blue
SEM	Scanning electron microscopy
PVA	Polyvinyl alcohol
PVB	Polyvinyl butyral
UV-VIS	Ultra-violet spectrophotometer

PENJERAP NIPIS UNTUK PENYINGKIRAN METILINA BIRU MENGGUNAKAN CARA BERUSAN, BERUSAN ANGIN DAN PEMUTARAN ELEKTRIK

ABSTRAK

Paintosorp^{TM} adalah satu penjerap inovatif yang dicipta untuk penyingkiran pewarna daripada air kumbahan industri. Fokus kajian ini adalah untuk mencari cara untuk menerapkan Paintosorp dengan menggunakan cara berusan, berusan angin dan pemutaran elektrik. Berusan angin menggunakan tekanan udara untuk mengecat Paintosorp^{TM} dalam bentuk titisan kecil dan pemutar elektrik menggunakan sumber elektrik yang tinggi untuk menenun penjerap menjadi serat bersaiz nano. Kebolehan penjerap yang dibuat menggunakan berusan angin dan serat PVB/Bentonite yang dibuat menggunakan pemutar elektrik telah diuji dengan pertukaran kadar pusaran magnet, pH dan kepekatan awal pewarna. Salutan penjerap berusan angin Paintosorp^{TM} mencatatkan kadar penjerapan tinggi dan sedikit terjejas dengan perubahan pH dan kepekatan awal perwarna. Paintosorp^{TM} telah mencatat kadar penyingkiran MB 100% untuk kedua-dua kepekatan rendah (20 ppm) dan tinggi (200 ppm) dalam masa 4 jam pertama dan ianya memberi kesan dengan kadar penyingkiran MB yang rendah apabila diuji dengan pH dan kadar pusaran berlainan. Keupayaan penjerapan Paintosorp^{TM} adalah 45.0 mg/g apabila diuji dengan kepekatan 200 ppm. Serat PVB/Bentonite telah mencatat kadar penyingkiran MB yang rendah apabila dibandingkan dengan Paintosorp^{TM} di mana ia hanya mempunyai kadar penyingkiran MB sebanyak 88% di kepekatan 20 ppm dan 33% di kepekatan 200 ppm. Keupayaan penyingkiran MB untuk serat nano adalah 47.7 mg/g apabila diuji dengan kepekatan 200 ppm. Pertukaran pH dan kepekatan awal pewarna memberi kesan yang jelas

dalam keupayaan penyingkiran MB. Serat PVB/Bentonite ini mempunyai kadar penyingkiran MB yang rendah apabila di dalam keadaan asidik dan kadar penjerapan jatuh apabila kepekatan meningkat. Apabila kepekatan meningkat dari 100 ppm ke 200 ppm, kadar penyingkiran MB jatuh daripada 47% kepada 33%. Kadar pusaran mencatatkan kesan yang rendah kepada keupayaan penyingkiran MB serat nano. Pencirian Paintosorp^{TM} berusan angin dan serat PVB/Bentonite dan serat nano telah dilaksanakan menggunakan SEM,EDX dan FTIR. Ia didapati bahawa serat PVB/Bentonite mempunyai lebih banyak liang apabila dibandingkan dengan Paintosorp^{TM} berusan angin tetapi Paintosorp^{TM} berusan angin mempunyai atom Al dan Si yang lebih banyak. Salutan penjerap mengikut isoterma Freundlich manakala serat nano mengikut isoterma Langmuir. Kajian kinetic menunjukkan bahawa kedua-dua salutan penjerap dan serat nano mengikut psuedo-tertib kedua.

THIN LAYER ADSORBENT FOR THE REMOVAL OF METHYLENE BLUE VIA BRUSHING, AIRBRUSHING AND ELECTROSPINNING

ABSTRACT

Paintosorp^{TM} is an innovative adsorbent coating that was designed for the removal of dyes from industrial wastewater. This research focuses on the methods of applying Paintosorp^{TM} and PVB/Bentonite via various methods such as brushing, airbrushing and electrospinning. Airbrushing uses air pressure to paint Paintosorp^{TM} in miniscule droplets meanwhile electrospinning utilizes high voltage to weave the adsorbent into nanofibers. The adsorption ability of airbrushed Paintosorp^{TM} and electrospun PVB/Bentonite nanofiber was tested with the change in stirring velocity, pH and initial adsorbate concentrations. Paintosorp^{TM} recorded high adsorption of 100% removal for both low (20 ppm) and high concentrations (200 ppm) in the first 4 hours of the experiment and is affected slightly with the change pH and stirring velocity. The adsorption capacity of airbrushed Paintosorp^{TM} were at 45.0 mg/g when tested with high concentration of MB of 200 ppm. The electrospun PVB/Bentonite nanofiber had lower removal compared to Paintosorp^{TM} where it had only 88% removal of MB at 20 ppm and 33% removal at 200 ppm. The adsorption capacity of the electrospun nanofiber were at 47.7 mg/g when tested with 200 ppm. The changes in pH and initial adsorbate concentrations had significant effect on its MB removal. The PVB/Bentonite nanofiber performs poorly in acidic conditions and the MB removal drops as the concentration increase from 100 ppm to 200 ppm, where the MB removal was at 47% removal to 33% removal respectively. The stirring rate only had slight effect on the nanofiber adsorption ability. The characterization of the airbrushed Paintosorp^{TM} coating and PVB/Bentonite nanofibers were done using SEM, EDX and

FTIR. It is found that the nanofiber were more porous than the coating but the coating had higher presence of Al and Si atoms. The airbrushed Paintosorp^{TM} coating fits the Freundlich isotherm model meanwhile the PVB/Bentonite nanofiber fits the Langmuir model. The adsorbent kinetics studies revealed that both the adsorbent coating and nanofiber fits the pseudo-second-order model.

CHAPTER 1

INTRODUCTION

1.1. Water and water pollution

Water are clear, tasteless, odourless substance that is essential for all forms of life and is an act as the universal solvent for many substances. Water is integral in the survival of a human being, apart from air and food. Of all the planets that exists in the solar system, the only planet that contains 73% of its surface covered in water is Earth, although 97% of the existing water is seawater and due to its high salinity, it is unsuitable for human consumption. The other 2.76% are fresh water out of which 2.4% is available and about 0.3% to 0.5% of it is available for drinking consumption. Water continuously change and constantly moving in a cycle called the hydrologic cycle (Dastrup, 2018). Water can be found in the ocean, atmosphere and on the surface. Water evaporates into the air as water vapour and condensed water vapour form precipitates into rain, or snow and goes back onto the Earth's surface. These precipitates fall into open bodies of water, absorbed by vegetation and become surface runoff and some are stored as groundwater. All the water then re-enter the ocean and continue the hydrologic cycle (Pagano & Sorooshian, 2014).

In the last century, the rapid growth of the world's population has severe effects on the resource use of Earth. The use of water was doubled in the 20th century when compared to the population growth. It is estimated in 2025, 1 800 million people will be living in absolute water scarcity, and two-thirds of the world population could be under stress conditions (Loucks & van Beek, 2005). Development of urban areas could worsen the estimated value as it would put pressure on the available water resources (Farha et al., 2012). Clean water supplies and sanitation persist to be a major problem in many parts of the world, with 20% of the global population lack access to safe drinking water. In developing countries, water-borne problems continue to plague the people and affects their health. Polluted water claimed many children lives annually (Loucks & van Beek, 2005).

Water pollution is mainly caused by wastewater, released by domestic, industrial agriculture, and transport use. The wastewater released by these sources affects the biotic and abiotic components of the ecosystem. Undesirable by-product released by industries undergo wastewater treatment before being released to a sanitary sewer or a surface water (Vunain *et al.,* 2016). Although treatment was done before release, some of undesirable by-product might slip away from the treatment and ended up released to the environment. Some of the pollutants that is released are such as organic compounds (benzene, chloroform, phenols and toluene), heavy metals (chromium, copper, lead and zinc), nitrogen compounds, natural and synthetic dyes and hydrocarbons.

1.2.Textile industry

The textile industry is a fast-growing industry in Malaysia. In the year of 2008, in the states of Kelantan and Terengganu, had produced close to 400,000 tonnes of man-made fibers, consisting of nylon, polyester filament, and staple (Pang & Abdullah, 2013). Considering the sheer amount of textile fibers produced, it is not surprising that it had significant effect on the environmental quality, with respect to the wastewater effluent.

Batik is one of the most recognized products from the Asian textile industry. Batik wastewater contains dyes originating from the dyeing process and in addition, the wastewater also contain synthetic ingredients that need to be degraded. In the colouring process, the compounds used in the dyeing process used about 5% of the primary compound and the other 95% was discarded as liquid waste (Sutisna et al., 2017).

The effect of textile industry operations have been studied numerously by various researchers. For example, textile effluent may contain suspended solids which can clog fish gills, risking the health and growth rate of the marine life. In addition, the dye released also reduce light penetration, and as a result, reduce the ability of algae to produce food and oxygen (Tüfekci et al., 2007).

1.3.Existing wastewater treatment methods

The industrial wastewater treatment plants have implemented numerous technologies to treat the effluents created before releasing the treated water to the environment. The said technologies can be generally classified into three categories, physical, chemical and biological. Physical method utilizes naturally occurring forces such as gravity and electrical attractions. It does not affect the chemical structure of the wastewater and some examples of physical methods used are sedimentation, filtration and adsorption. Chemical method uses chemical reactions to influence the wastewater. The examples for this method are chlorination, precipitation and chemisorption. Lastly, biological method uses bacteria and small organisms to break down the organic waste using cellular process (Pang & Abdullah, 2013). This method can be divided into aerobic and anaerobic processes.

1.4.Adsorption film/coating

The research on films or coatings is usually is for the application of medical treatments, scaffolding, and thermal barriers aesthetics. The use of film as adsorbents is still a niche application as the research on this is quite new. Up to recent years, the treatment of coloured wastewater had been dependent on the aerobic digestion (Buchanan, 2006), membrane separation (Gao, 2016), coagulation and flocculation (Prakash et al., 2008), trickling filtration (Daigger, 2012), ion exchange (Raghu & Ahmed Basha, 2007) and membrane bioreactor (Reif et al., 2011). These methods had been extensively used in industries, but each process faces technical and economical barriers.

An adsorbent coating is very versatile. Kadir et al., (2017) used surfactant modified bentonite adsorbent coating to soften hard water. The process of softening hard water is removing Ca^{2+} and Mg^{2+} ions. This coating was able to reach 66.67% removal efficiency of Ca^{2+} and Mg^{2+} ions from synthetic hard water.

An adsorbent coating that is able to remove methylene blue from water was developed by Azha et al., 2017 called Paintosorp™. This newly developed adsorbent coating utilizes water-based paint, bentonite clay and water to produce a slurry that is applied to a cotton fiber. It is a low cost and has high adsorption capability. This product has also been further research upon by Hamid, (2017) where the use of fin system and the mathematical formulae was researched upon. The fins function as the medium for the adsorbent coating and it is capable to remove up to 90% of methylene blue from the water. Paintosorp™ is created by mixing white water-based paint with bentonite into a slurry. The slurry is then applied onto a white cotton substrate via brushing or airbrushing. After the coating process, the coating is dried in an oven to ensure that it is fully dried.

1.5. Electrospinning

Nanofibers structures are desirable for the application of adsorption such wound dressings, scaffolding, membrane separation and drug delivery. There have been research on using electrospinning to produce an adsorbing-capable nanofibers. Deng et al.,(2011) implemented co-electrospinning in order to produce a nanofiber that is able to adsorp lead (II) ions. Co-electrospinning is a process where requires a polymer to be the shell and the other polymer, nonpolymeric Newtonian liquid or powder to fill the core. (Bazilevsky *et al.*, 2007). In addition, Haider & Park, (2009) studied electrospun chitosan nanofibers for the adsorption of Cu(II) and Pb(II) ions. The characteristics of electrospun nanofibers are desirable as they are highly porous, with high surface area to volume ratio, and has interconnected open pore structures which can offer reliable removal of pollutants from water (Aluigi et al., 2014). The nanosized fibers formed by electrospinning has better capability to collect particles because the flow slip between the fiber increases the diffusion and contact time.

Electrospinning is a versatile process that is capable of producing ultrafine fibers. The advantage of electrospinning is that the process is relatively quick and simple. Its ability to fabricate nanofiber from a variety of materials is also an advantage. The electrospinning process implement the self-assembly process which is induced by electromagnetic forces. The electrical charge enables the drawing of fibers from a polymer solution. A high-voltage power supply generates an electrical field between the needle tip to the collecting drum. A polymer drop forms on the tip of the needle, thus creating a Taylor's cone in the presence of the electrical field and from there, fluid jets is form from the apex of the cone. As the charged jet travels through the electrical field, the diameter of the jet decreases due to high extension rate and evaporation of the solvent (Svrcinova et al., 2010).

The study of electrospinning usually focused on four factor that affect the creation and quality of produced nanofiber. The polymers' molecular weight, topology and weight distribution are its factors. Next is the solvent for the polymer, where its surface tension, solubility parameter and relative permittivity play the major role in the mixing and spinning process. The produced polymer solution viscosity, concentration and specific conductivity is the other factor. The last factor is the process parameter of the electrospinner where the electric field strength, tip-to-collector distance, temperature and humidity (Huang *et al.*,2003).

Polyvinyl butyral is a well-established polymer that had been extensively used in the production of nanofibers. It has been used in the production of thermoelectric green tapes where the PVB acts as the binder (Salam *et al.*, 2000).

1.6. Problem statement

Paintosorp^{TM} is a thin coated adsorbent layer, a new type of adsorbent coating that was designed for the removal of dye from wastewater . It has been proven to have high adsorption capability and has potential to be used in industries. In spite of that, the process of applying the adsorbent via brushing could cause limitations in the adhesive strength and the thickness of the adsorbent. In addition, the management of waste fom the existing method could become costly.

A study on other possible methods of applying the adsorbent is important. Several other methods such as airbrushing and electrospinning can be implemented. The adsorption capabilities of these methods would be tested via vigorous stirring, acid and basic conditions and at different adsorbate conditions. Moreover, the result from the experiment will be used in equilibrium and kinetic studies to investigate the behaviour of the adsorbate with the adsorbent coating and nanofiber. Thus, this present work researches on the feasibility of other methods of applying Paintosorp^{TM} for the treatment of methylene blue.

1.7. Research objectives

The objectives of this research are to find new ways to apply Paintosorp^{TM} and PVB/Bentonite for the removal of MB. The adsorbent coatings made via brushing and airbrushing and adsorbent nanofibers made via electrospinning is tested with methylene blue dye. The specific objectives are as follows:

1. To analyse the parameters that affects the adsorption of MB for adsorbent coating and adsorbent nanofiber (adsorbate concentration, stirring velocity, and pH)
2. To identify the adsorption capacity of the adsorbent coating and nanofiber via different methods of application (Brushing, airbrushing and electrospinning)
3. To characterize the coatings and nanofibers and correlate the findings with the adsorption mechanisms.

1.8.Scope of study

The first stage of the study covers the screening study of methods of applying coatings. The aim of this study is to determine whether there are other methods to applying coating other than brushing. Three methods were studied, brushing, airbrushing, and electrospinning. The study on these methods were done by comparing their adsorption capabilities, adhesion strength, adsorbent concentrations and acidic/basic conditions.

Further study was conducted in the use of electrospinning. The thermoset nature of Paintosorp^{TM} may inhibit its spin ability. In this study, the interest was focusing on determining a new binder that would be able to support the adsorbent. Polyvinyl aniline and polyvinyl butyral were used as new binders. The binders were studied on the spinning time, water-resistance, and nanofiber strength.

The next stage of the study is to characterize the coating and nanofiber via Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Analyzer (EDX) and Fourier Transform Infrared (FTIR). The surface of the coating and nanofibers can be determined via these methods. Lastly, the adsorption result was then used in equilibrium and kinetic studies to investigate the behaviour of the adsorbate with the adsorbent coating and nanofiber. A batch adsorption study were conducted using different adsorbate concentrations, acid/basic conditions, vigorous stirring and polymer concentration.

1.9.Organization of thesis

This thesis comprises of five chapters, each providing details and data that was obtained from the research. The first chapter provides a brief introduction on the importance of water and the water pollution that plagues the rivers and other water bodies. In addition, this chapter also provide information on the textile industry and its effluents. Other than that, the use of adsorption coating can also be found with addition to the use of electrospinners. This chapter also consists of the problem statement that give weight to this research. The objectives of this research were made with relation to the research scope. The organization of this thesis is summarized in this chapter.

Chapter 2 covers the study on the characteristics of dyes, methylene blue dye specifically. It covers the use and impact of methylene blue dye to people and to the environment. After that, a brief summary of existing dye treatments that consist of physical, chemical and biological methods. The next subchapter is about the adsorption mechanism and the parameters that affect it. Several research papers were studied in this subchapter. Next, the use of bentonite as the adsorbent is shown. In addition, the type of binders which are water-based paint, polyvinyl aniline (PVA) and polyvinyl butyral (PVB) is also studied. Finally, an overview of the application method of Paintosorp^{TM} and its variant.

The materials and methods used in this research is compiled in chapter 3. The details of the chemicals, equipment, materials and experimental procedure are stated and arranged accordingly. This chapter provides the adsorbent coating and electrospinning procedure and the batch adsorption experiment. The equations for the equilibrium and kinetic study is also provided here.

The results from the experiment is compiled and discussed in chapter 4. The results are presented in the form of figures, graphs and tables. The results were discussed from the perspective of the adsorbent performance, adsorbent surface, and equilibrium and kinetic studies.

Chapter 5 is the final chapter of this thesis. It covers the overall conclusion of the findings based on the objectives. Several recommendations is stated here for further improvement in the future.

CHAPTER 2

LITERATURE REVIEW

2.1. Introduction

This chapter reviews the understanding of the adsorbate, adsorbent and adsorption process. It also includes the types of existing wastewater treatment methods and the adsorbent application methods. Other than that, the equations used in the adsorption isoterms and kinetic studies is also inside this chapter.

2.2. Dyes

Dyes differs from other organic compounds as they are able to possess colour, which is caused dyes being are able to absorb light in the visible spectrum (Carreón-Valencia et al., 2010). The use of dyes could be traced back far into history. Dyed fabric from thousands of years ago have been discovered in Egyptian tomes and it is discovered that the dyes were manufactured from natural sources such as berries, fruits, nuts, blossoms, leaves, stems, roots, bark and twigs. These dyes can be considered as natural dyes, and were extensively used before the discovery of synthetic dyes by William Henry Perkin (Nagendrappa, 2010).

The production line of the textile, leather, pulp and paper and plastic industries utilizes dyes to colour their products. Thus, the wastewater effluent released by those said industries may cause environmental problems. There are 40,000 types of dyes and pigments with various chemical structures that made them chemically, physically, photolytically and biologically stable. The type of dye that is used in the modern industry are synthetically produced as synthetic dyes are cheaper than natural dyes, lasts longer, and has a wider range of colour choices. However, the industries use abundant amount of water for their processes, and ended with creating a huge amount of coloured wastewater to be processed. Even a very small concentration may change the colour of the water and it is aesthetically unpleasant for the public to see and it also interferes light penetration and reduces photosynthetic activities (Ponnusami et al., 2008).

The chemical composition and its colouring particles differentiate the types of dyes. Dyes are a compound that contain chromophore and auxochrome groups. The chromophore group affect dye colour via saturation and auxochrome group affect the dye fiber reaction. Dyes can be obtained naturally or synthetically made. Synthetic dyes can be classified into several classes as depicted from Table 2.1 below:

Table 2.1 : Type of dyes, chemical structure, affinity, properties and suitable application (Carreón-Valencia et al., 2010)

Synthetic dye type	**Chemical Structure**	**Affinity**	**Properties**	**Application**
Direct	Azo group	Hydrogen bonds Van der Waal forces	Soluble in water Negatively charged	Rayon Silk Wool Cotton Linen
Acid	Aromatic rings Sulphonyl group Amino group	Hydrogen bonds Van der Waal forces Ionic bonds	Soluble in water Negatively charged	Wool Silk Polyamide Modified acrylics
Basic	Sulphonate group Carboxylate group	Ionic bonds	Soluble in water Positively charged	Wool Silk Acrylic
Azoic Dye	Azo group Aromatic rings	Physical entrapment	Insoluble in water Neutral	Cotton Viscose
Vat Dye	Quinone	Physical entrapment	Insoluble in water Neutral	Cotton Linen Rayon Wool

Table 2.1: Cont.

Synthetic dye type	Chemical Structure	Affinity	Properties	Application
Mordant Dye	Hydroxyl group Carboxyl group Metal atoms	Ionic bonds	Soluble in water Negatively charged	Silk Wool Polyamide
Reactive Dye	Hydroxyl group	Covalent bonding	Soluble in water Negatively charged	Cellulosic fiber Wool Nylon
Sulfur Dye	Sulphur Polysulphide	Physical entrapment	Insoluble in water	Cotton Viscose
Solvent Dye (Koh, 2011)	Anthraquinone Azo group Quinine group Nitro group	Adsorption Diffusion	Very low solubility in water Neutral	Cellulose ester Acetate fiber Polyester fiber

2.3. Methylene blue

Methylene blue (MB) dye is a cationic dye which has various applications in chemistry, biology, medical science and dyeing industries (Pathania et al., 2017). It is a heterocyclic aromatic compound with a molecular formula $C_{16}H_{18}N_3SCl$. Figure 2.1 shows the molecular structure of MB.

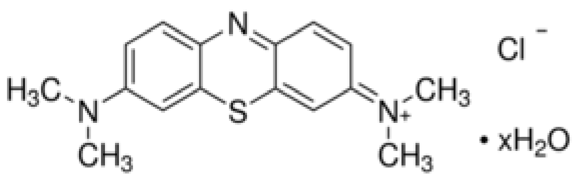

Figure 2.1 : Methylene blue molecular structure

MB is a basic dye, which has been used for dyeing wool and silk in the textile industry and even used in the medical fields to inspect some diseases (Abdellah et al., 2018). MB had been used in both human and veterinary medicine in therapeutic and diagnostic procedures (Fil et al., 2012).

Methylene blue is a monoamine oxidase inhibitor thus could have on an impact on human health if the dosage is high (Ramsay et al., 2007). Jia et al., 2018 reported that uncontrolled release of MB into the surface and underground water could harm living beings as its toxicity affect the neural tissue, reproductive organs and the skin.

2.4. Existing methods to treat wastewater

There are numerous ways for the treatment of wastewater. In general, those treatments can be divided into three groups, physical, chemical and biological methods.

2.4.1. Physical treatment

Physical methods of wastewater treatment accomplish substance removal by utilizing naturally occurring forces, such as gravity, electrical attraction, and van der Waals forces. Physical barriers are also utilized in this treatment method. Physical process in general does not affect the chemical structure of the targeted wastewater. The several examples of physical treatment are sedimentation, filtration and adsorption. Sedimentation is the partial separation of suspended solid particles from a liquid by gravity settling. It is affected by particle size, liquid viscosity and the densities of the solid and the solution (Cancino-Madariaga & Aguirre, 2011). The weakness to this method is that it is considered slow and requires the use of expensive flocculants to facilitate the aggregation of small particles into larger agglomerates (Niaounakis & Halvadakis, 2006). Filtration is a process to remove particles from suspension in water. The mostly used filtration method used on dyes is the membrane filtration method. However, this method has presented disadvantages in the low rejection factors, limitation in pressurized conditions and fouling formation (Laqbaqbi et al., 2019). Adsorption is the adhesion of atoms, ions or molecules from a gas, liquid or dissolved solid onto a surface. In the wastewater treatment processes, the adsorption process is one of the most attractive method that have been used by industries due to its ease of operation, simplicity and lack of by-product generation (Aljlil & Alsewailem, 2014; Azha et al., 2017; Hong et al., 2009; Li et al., 2011; Peng et al., 2017).

2.4.2. Chemical treatment

Chemical treatment consists of using chemical reactions in order to improve water quality. One of the chemical methods used is the chlorination method. Chlorination is a process where oxidation decolourize the wastewater. However, this results in formation of by-products from the oxidation process which can affect the health of humans (Khan et al.,2014). Other than that, one of the other ways is the coagulation precipitation method. It is a physicochemical treatment procedure that through the addition of chemicals and chemical reactions, forms an insoluble end product that can be removed from the wastewater. This method heavily depends on the characteristic of the raw wastewater, pH and temperature of the solution, type and dosage of coagulants which can be costly (Sabur et al., 2012).

2.4.3. Biological treatment

In biological wastewater treatment, generally the process is divided into two processes in which anaerobic process is first and aerobic process is second. The anaerobic process takes a longer time when compared to aerobic process and the anaerobic bacteria is very fragile, and it can be easily agitated causing poor treatment performance.

2.5. Adsorption

Adsorption is a phenomenon where molecular species deposits on the surface of the adsorbent. The adsorbent is where the adsorption process occurs and the adsorbate is the molecular species that is adsorbed. Adsorption is also based on the strength of the interaction between the adsorbent and the adsorbate. Desorption is the release of the adsorbate from the adsorbent, and it occurs when the equilibrium is disturbed.

The adsorption mechanism can be divided into three steps. It starts with the diffusion of adsorbate to the adsorbent surface. It continues with the migration of the adsorbate in the pores or the active sites of the adsorbent. The pores of the adsorbent play a major role as the most of the adsorption process occurs here. Lastly, when the adsorbate molecules are distributed on the surface of the adsorbent and the adsorbent pores are filled up, the particles of the adsorbate build up the monolayer of reacted molecules, ions and atoms to the active sites of the adsorbent (Musin, 2013). Figure 2.2 shows the adsorption mechanism process.

Adsorption occurs in several situations that is when the adsorbate has low solubility in the waste, compatible affinity of the adsorbate with the adsorbent or in the combination of the two.

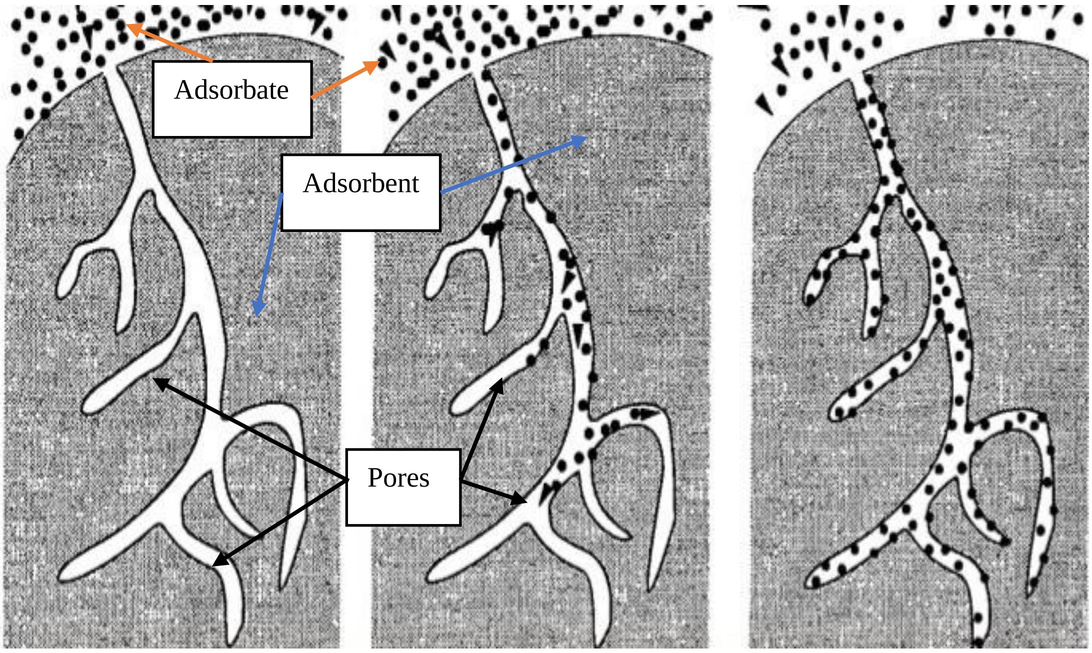

Figure 2.2 : Adsorption mechanism (Musin, 2013)

2.6. Types of adsorption

There are two types of adsorption which depends on the type of attraction between the adsorbate and the adsorbent, that is physical and chemical adsorption. Physical adsorption relies on force of attraction such as van der Waals forces, which is a weak force and chemical adsorption relies on chemical bonding between the molecules and it is a strong force of attraction. Table 2.4 shows the comparison between these two adsorption types (Atkins *et al.*,, 2018)..

Table 2.2 : Comparison between physical and chemical adsorption

Physical adsorption	Parameter	Chemical adsorption
Exothermic Low enthalpy value Van der Waals force Low activation energy requirement Reversible process	Energetics and kinetics	Exothermic High enthalpy value Chemical bonding High activation energy Irreversible
Can occur at lower temperature Adsorption drop as the temperature increase	Effect of temperature	Extent of adsorption increase as the temperature increase but up to a certain limit before adsorption start decreasing
Adsorption of gases over solid increases with pressure as gas volume decrease	Effect of pressure	Not affected by small changes in pressure Favourable in very high pressure
Does not have specificity as the van der Waals' forces are universal	Specificity	Very specific to the compatibility of the adsorbent and the adsorbate
Extent of adsorption increase as the surface area increase	Surface area of adsorbent	Extent of adsorption increase as the surface area increase
20 - 40	Heat of adsorption (kJ/mol)	40 – 400

Adsorption are affected by several factors and below explain its effects (Atkins *et al.*,, 2018).

1. Surface area

   Adsorption is a surface phenomenon and thus the adsorption rate is proportional to the specific surface area.

2. Nature of adsorbate

   Adsorption increase with the decrease of solubility of the solvent. The adsorption rate of the adsorbate and its solubility in the solvent increase as the solubility of the solvent decrease.

3. pH

   The degree of hydrogen and hydroxide ions affect the pH of the solution. Adsorption rate is highly influenced with pH as hydrogen and hydroxide ions are adsorbed strongly, and it affects the adsorption of other ions.

4. Temperature

   Adsorption is usually greater at high temperatures but it does not affect on the adsorption equilibrium and thus small variations in temperature do not alter the adsorption process to any significance.

5. Mixed adsorbates

   The interaction of mixed adsorbates may affect each other. It may mutually enhance adsorption, act independently, or even inhibit each other. The affinity of the adsorbate with the adsorbent, concentration of adsorbates, molecular sizes affect the degree of mutual inhibition of the adsorbates.

6. Nature of adsorbent

   The physicochemical nature of the adsorbent has significant effect on the adsorption rate and adsorption capacity. The structural detail and surface functional group affects the adsorption capability.

2.7. Adsorbent

Adsorbent are surfaces where adsorbates adsorb to. The adsorbent material favourability depends on its physicochemical properties such as specific surface area, ion exchange capacity, adsorption affinity and pore size (Budsaereechai et al., 2012). In addition, good low-cost adsorbents are important for the sustainability of the environment. Using low cost adsorbents helps in waste minimization, recovery and reuse(Ali et al., 2012). An effective adsorbent is an adsorbent that has high adsorption capacity and cost-effective (Akpomie & Dawodu, 2015). Adsorption techniques that utilizes clay minerals as adsorbents are relatively inexpensive and has high efficiency (Pawar et al., 2016).

2.7.1. Activated carbon

Activated carbon (AC) is one of the most widely used adsorbent due to its high adsorption capacity, effectiveness, surface area and large pore volume(Kibria, Pal, Mizuno, & Saha, 2016). Adsorption of dyes from aqueous solution require AC to have not only large capacities but in addition significant pore volumes and surface areas contributed by mesopores due to the large dye molecules (Tan et al., 2008). In recent times, most of the activated carbon are created from the by-products of the agriculture. The abundance and availability of these by-products made them good sources of raw materials.

Commercially available activated carbons are relatively expensive thus restricting its usage in the adsorption application. This is mostly due to the amount that has to be used for large scale removal of dyes. The quality of the commercial activated carbon also increases the cost as the quality increase. It is also non-selective and ineffective against disperse and vat dyes (Demirbas, 2009). The cost for regeneration of the saturated carbon is also expensive, not straight-forward and also cause the loss of the adsorbent. In order to combat this predicament, researchers have studied on the development of low cost adsorbents that uses the agricultural wastes (Li *et al.*, 2016; Noor *et al.*, 2017; Ponnusami *et al.*, 2008; Tan *et al.*, 2008). Li *et al.,* (2016) utilized biochar from wheat straw to adsorp MB. Meanwhile, Noor *et al.,* (2017) utilized sugarcane bagasse to adsorp metal ions. Ponnusami *et al.*, (2008) and Tan *et al.*, (2008) used guava leaf powder and coconut husk respectively for the removal of dyes.

2.7.2. Bentonite

Bentonite is a raw material composed of montmorillonite and clay minerals of the smectite group. Montmorillonite is a 2:1 type mineral and its unit layer structure consists of one Al^{3+} octahedral sheets (Alexander et al., 2018). The charge between the octahedral and tetrahedral sheets are not balance due to the isomorphous substitution of the ions in its specific sheets. The substitution of the ions induces a negative charge on the bentonite. The substitution event can be seen in Figure 2.3 with credit to (Hebbar et al., 2014). The negative charge is weak and the cations can be adsorbed to the specific hydration shell. The cations can also be replaced by ion exchange.

The porous structure of bentonite can be classified into three categories that are micropore, mesopore and macropores. The adsorption capacity of bentonite depends on the micropores and mesopores. The ability of bentonite to act as an adsorbent for wastewater treatment such as methylene blue and heavy metal ions have been proven by several researchers (Auta & Hameed, 2014; Chinoune *et al.*, 2016; Hong *et al.*, 2009; Liu *et al.*, 2014; Pawar *et al.*, 2016; You *et al.*, 2017).

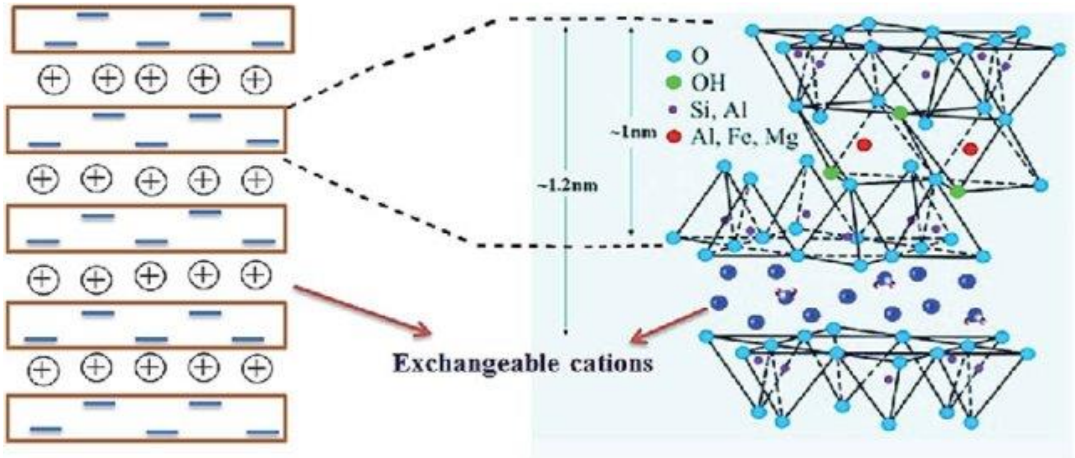

Figure 2.3 : Bentonite structure (Hebbar et al., 2014)

Studies have found that the adsorption rate is heavily influenced by solution pH, initial adsorbate concentration, contact time and temperature (Dai *et al.,* 2018). Modification made onto bentonite by De Castro *et al.,* (2018) into acid-modified bentonite found that it could increase the adsorption rate of bentonite when compared to unmodified bentonite. The modification changed the bentonite from aggregated flakes to larger aggregates, where the particle size increase. Table 2.3 shows the previous findings by several researchers.

Table 2.3 : Adsorption of different adsorbates with bentonite

Adsorbate	**Performance (q_e)**	**Reseacher**
Copper and Nickel ions (30 ppm)	Cu = 13.22 mg/g Ni = 9.29 mg/g	(Aljlil & Alsewailem, 2014)
Atrazine (1000 ppm)	Atrazine = 267.85 mg/g	(Ajala *et al.*, 2018)
Methylene Blue (175 ppm)	MB = 5.25 mg/g	(Hong et al., 2009)
Procion Blue and Brilliant Blue (100 ppm)	PB = 39.63 mg/g BR = 42.52 mg/g	(Chinoune et al., 2016)
Methylene Blue (250 ppm)	MB = 52.63 mg/g	(Azha *et al.*,2017)
Methylene Blue and Copper ions	MB = 160 mg/g Cu = 27 mg/g	(De Castro et al., 2018)

2.8. Binders

Binders or resin are the polymer that form a matrix to hold the pigment in place (Selinger & Barrow, 2017). The binder provide protection to the substrate and the components within the film. The binder also ensures the filler and pigments are homogenously dispersed and influences the durability, flexibility and its toughness of the binder. The quantity used for the binder is imperative in order to control the adhesive strength of the binder and ensure that the paint is not too brittle after drying.

2.8.1. Emulsion paint/Water-based paint

Emulsion paint are water-based paint (Selinger & Barrow, 2017). Normally, emulsion paints used acrylic polymers as its binder. The components of the binder are based homo and co-polymers of vinyl acetate and propenoate ester. It is called emulsion paint due to a process called emulsion polymerization. It is a process where the liquid monomers to be polymerized are dispersed in water.

The drying process of water-based paints consists of two phases, evaporation and coalescence. Evaporation is when the volatile liquid evaporates from the paint film. The water evaporates first as the other co-solvents are designed to stay in the film for an extended duration. The evaporation of water causes the wet paint to shrink, forcing the particles of the paint to come together and overcome their mutual repulsion. Coalescence occurs after all the volatile liquids have evaporated, forming a coherent paint film. Mutual attraction takes place in this phase, forcing any remaining water or coalescent solvent to be removed from the film. The process continues until the polymer fuse together and forming a continuous film of polymer. After the water and coalescent solvent evaporates, the paint film becomes insoluble in water.

2.8.2. Polyvinyl alcohol (PVA)

Polyvinyl alcohol is a water-soluble polymer that has good chemical and thermal stability. It is non-toxic and biocompatible. It is also has high water permeability and can be processed easily (Guo et al., 2013). PVA is a semi-crystalline polymer that can easily form a hydrogel by repeated freeze-thaw cycles without the implementation of chemical crosslinkers. The hydroxyl groups in the main chain of PVA are able to become the source of hydrogen bonds which assists in the formation of hydrogel composites (Dai et al., 2018). The super-paramagnetic iron oxide nanoparticles

(SPIONs)/gelatin(gel)/polyvinyl alcohol(PVA) nanoparticles were developed by Dolgormaa et al., (2018) were designed to adsorb Cu^{2+} and Zn^{2+} from aqueous solution. The SPIONs were prepared by co-precipitating iron (II) and iron (III) in ammonia solution. It was then treated with gelatin and PVA to form the nanoparticles. The nanoparticles were rich in different functional groups and were very suitable for chemisorption. The PVA were added for stability and enhancing the adsorption ability of the nanoparticles.

Several researchers have implemented PVA into their research (Dai et al., 2018; Guo et al., 2013; Sarhan & Azzazy, 2015; Toader et al., 2016; Wang & Wang, 2017). Most of these researchers implemented PVA with other materials in order to improve the water resistance strength of PVA. PVA is a very hydrophilic polymer so the risk of the polymer to dissociate in water is very high. Some researchers also implemented crosslinking process into the fabrication process in order improve the linking strength between the nanofibers. The nanofiber made from PVA and silica by Wang & Wang, (2017) implemented the pore making process to increase the surface area and mesopore volume of the nanofiber. Other than that, an electrospun nanofiber by Sarhan & Azzazy, (2015) were made out of chitosan, honey and PVA. The nanofibers were prepared with different compositions of chitosan, honey and PVA and the solvent used were acetic acid. The polymer was electrospun and the fiber mats undergone a cross-linking process. Both physical and chemical cross-linking were implemented to increase the water-resistance strength of the polymer.

2.8.3. Polyvinyl butyral (PVB)

Polyvinyl butyral (PVB) is a non-toxic, odourless and environmentally friendly hydrophobic polymer. It also have flexibility, optical clarity and good adhesive strength(Yener & Yalcinkaya, 2013). PVB is synthesized from PVA and butyraldehyde in an acidic condition. PVB is found to be polyhydroxy and polyacetal, where it contains a significant proportion of butyral, hydroxyl and acetyl functional groups. The vinyl alcohol group of PVB is hydrophilic meanwhile the vinyl butyral group is hydrophobic. The differing nature that exists in PVB make it compatible with both polar and non-polar components of other additives (Kumar et al., 2016).

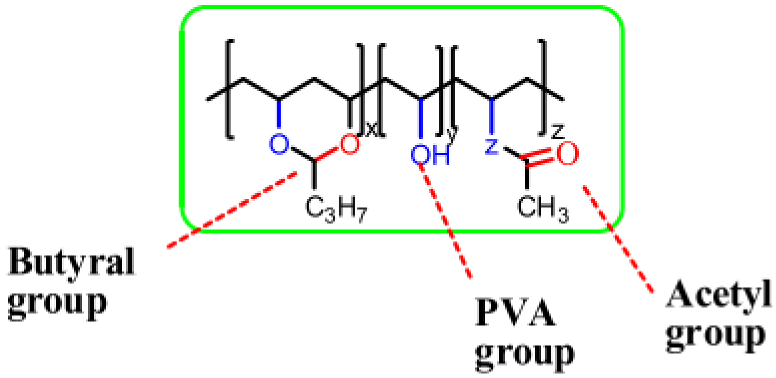

Figure 2.4 : Molecular structure of Polyvinyl Butyral (Kumar et al., 2016)

PVB had been used in studies and some have used it in the formation of electrospun nanofibers and films (Ahmed Ben Hassan et al., 2014; L. Chen et al., 2009; Peer et al., 2014; Salam et al., 2000; Yener & Yalcinkaya, 2013). A study of the effect of different solvents on PVB in which the polymer is used in electrospinning was studied by Yener & Yalcinkaya, (2013). They found that the good solvents to dissolve PVB is in propanol and ethanol with the positive impact on the electrospinning process. The fibers formed from these solvents were able to create uniform fibers and better fiber diameter distribution with lesser amount of bead formation. PVB/Silica nanofibers were synthesized by L. Chen et al., (2009) where they researched on the feasibility of using electrospinning to create a nanofiber mat that has a large surface area that could provide high sensitivity and fast response time in sensing applications. Electrospun zirconium hydroxide nanoparticle fabrics had used PVB as the binder and